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DECORATION OF GLASS AND GLASS ARTICLES USING THE PLASMA-SPRAYING METHOD

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Results of a study of plasma spraying of glass powders on glass substrates are described. It is demonstrated that decorative plasma treatment of glassware produces a coating of a granular structure with good consumer properties.

Traditional methods for household-glass decoration involve lengthy firing needed to fix the applied pattern [1]. In employing these methods, a paste or silicate paints are usually applied by hand. The low efficiency and high labor intensity of these processes increase the production cost of the articles.

A substantial shortcoming of the traditional methods consists in the impossibility of applying materials with a melting point or T_g exceeding T_g of the glass material. It narrows the range of materials suitable for decoration. Decoration by plasma spraying makes it possible to intensify the process, avoid a lengthy firing stage, and apply decorative materials whose melting point and T_g are higher than T_g of the substrate.

There are virtually no data on deposition of glassy decorative coatings on glass articles using the plasma-spraying method [2, 3].

The present paper describes results of a study of the technological parameters of plasma spraying that form the consumer properties of decorative coatings.

Spraying was performed using the following glass powders: colorless household glass; chromium-colored green household glass; lead crystal; selenium-ruby household glass; black and blue marblite; sheet glass (Table 1). The glass substrates were household glassware (liqueur glasses, wine glasses, goblets), heat-resistant kitchenware (pans and bowls), and sheet, plate, figured, and armored glass. The glass powders were fed to a GN-5R torch of a UPU-8M

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TABLE 1

Glass	Weight content,* %										
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	ZnO	B_2O_3	Fe_2O_3	F
Lead crystal	56.5	0.5	–	–	1.0	15.0	0.4	1.8	1.2	0.024	–
Selenium-ruby household glass	66.5	1.0	–	–	13.0	6.0	0.4	8.0	3.5	0.05	–
Chromium-colored green household glass	72.7	–	6.8	2.0	15.0	2.0	0.5	–	1.0	0.05	–
Marblite:											
black	65.3	2.8	6.6	–	18.5	–	–	–	–	–	2.0
blue	64.93	3.97	7.1	–	16.5	–	–	–	–	–	7.5
Colorless household glass	71.0	1.0	6.0	–	13.0	4.0	0.5	–	–	–	–
Sheet qlass	72.5	1.0	9.0	3.0	14.0	–	0.4	–	–	0.1	–

* The content of PbO in lead crystal was 24.0%, the Cd content in household glass (selenium ruby) was 0.5%, the Se and Cr_2O content in green household glass was 0.5 and 1.0%, respectively, the content of Mn_2O_3 in black marblite was 4.8%, the content of Sb_2O_3 in blue marblite was 0.1%, and the BaO content in clear household glass was 4.5%.

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plasma gun using a special compressor-operated feeder. The plasma-gun power was varied from 12 to 24 kW. Argon acted as the plasma-forming gas; its consumption was 0.00093 – 0.00140 g/sec under a pressure of 0.24 – 0.26 MPa. The distance between the plasma-torch nozzle and the glass-product surface was varied within the range of 200 – 350 μm depending on the operating parameters of the plasma gun. The general scheme of the decorating process is shown in Fig. 1.

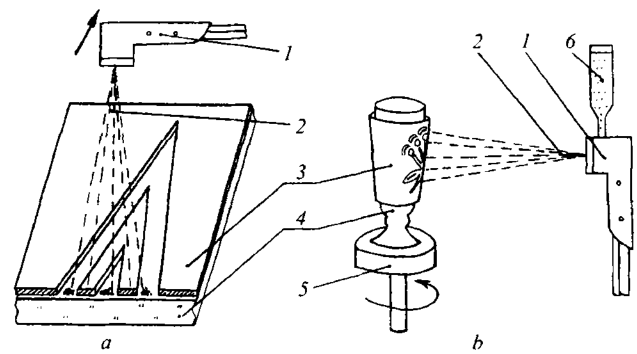

Fig. 1. Decoration scheme for sheet glass (*a*) and household and heat-resistant glassware (*b*): *1*) plasma torch; *2*) flow of melted glass particles; *3*) stencil; *4*) glass article; *5*) rotating tournette; *6*) glass powder.

The shape of the sprayed-powder particles should be nearly spherical, and the powder should have a strictly specified granular composition. A difference in particle sizes results in the fact that some particles evaporate, others melt completely, and still others become partly fused and have a negative effect on the coating quality [4].

The selection of the granular composition of glass powders for plasma spraying should be based on the following principle. The amount of heat transferred by a particle melted in the plasma torch to the point of contact with the glass-article surface should be sufficient for softening the surface layer of the glass. At the same time, no microcracks should appear in the glass. Therefore, it is expedient to use glass powders of a strictly specified granular composition. In order to reduce the severity of the thermal shock, the substrate should be preheated. This requirement does not extend to heat-resistant glasses with increased heat stability.

It was experimentally established that the particle size of powders suitable for plasma spraying has a range from 80 to 250 μm, depending on the chemical composition. Preheating of the glass substrate to a temperature of 523 K prevents the appearance of microcracks in deposition of the indicated glass-powder fractions [2]. A glass powder with a particle size below 80 μm is unacceptable for spraying on a glass substrate even if the latter is heated to T_g. This is due to the fact that grains of size below 80 μm cool at a distance of ~300 mm from the plasma-torch nozzle and do not reach the substrate in consequence of being captured by effluent flows of the plasma-forming gas.

Glass powders whose particles are larger than 250 μm are not suitable for spraying for the following reasons. First, if these large particles are not melted while they stay inside the plasma torch, the coating does not adhere to the glass base. Second, if they are melted, microcracks appear at the site of their contact with the substrate due to the substantial thermal shock.

Glass powders subjected to plasma treatment altered their chemical composition. Thus, the investigated glass compositions were enriched in calcium and silicon oxides and depleted in sodium and potassium oxides. The lead crystal was depleted in lead oxide, and the selenium ruby was decolorized due to decomposition of the CdS · SeS coloring complex and partial evaporation of the selenium (Table 2). Partial evaporation of the alkali-earth oxides and enrichment of the considered glasses with silicon and calcium oxides in-

TABLE 2

Glass	Weight content, %											
	CaO		SiO_2		Na_2O		K_2O		PbO		Se	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Lead crystal	–	–	56.5	57.8	1.0	0.97	15.0	14.87	24.0	21.5	–	–
Selenium-ruby household glass	–	–	66.5	67.1	13.0	12.1	6.0	5.82	–	–	0.5	0.4
Chromium-colored green household glass	6.8	7.1	72.7	73.5	15.0	14.1	2.0	1.85	–	–	–	–
Marblite:												
black	6.6	6.79	65.3	66.8	18.5	17.1	–	–	–	–	–	–
blue	7.1	7.22	64.93	65.95	16.45	15.9	–	–	–	–	–	–
Colorless household glass	6.0	6.6	71.0	71.8	13.0	12.3	4.0	3.8	–	–	–	–
Sheet glass	9.0	9.7	72.5	73.3	14.0	12.9	–	–	–	–	–	–

TABLE 3

Glass	T_g, K		T_f, K		TCLE, 10^{-7} K^{-1}		Refractive index		Microhardness, kgf/mm^2	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Lead crystal	741	819	766	841	109.4	103.6	1.544	1.534	497	521
Selenium ruby household glass	759	825	787	845	105.1	102.5	1.531	1.523	512	535
Chromium-colored green household glass	778	812	838	872	103.7	96.2	1.524	1.520	507	528
Marblite:										
black	753	821	782	841	94.0	90.7	1.512	1.503	485	516
blue	768	829	798	868	96.3	91.8	1.522	1.514	490	520
Colorless household glass	833	852	894	916	93.7	89.0	1.502	1.490	548	567
Sheet glass	863	889	910	927	89.0	87.4	1.531	1.527	520	541

creased their chemical stability. This was indicated by experiments performed to determine the water resistance by boiling the glass in water with subsequent titration in a 0.01 N solution of hydrochloric acid [5].

The values of the TCLE, T_g, and T_f of the glasses before and after plasma treatment were determined using the standard methods [6]; the refractive index was determined by GOST 26822–86, and the microhardness was measured on a PTM-3 device. The properties of the investigated glasses are given in Table 3. It can be seen that after plasma treatment T_g and T_f of the glasses shift to a higher-temperature region, the TCLE decreases, the microhardness increases, and the refractive index is altered.

Before spraying the glass powders, a stencil made of copper or aluminum foil was placed on the household and heat-resistant glassware (glasses, wine and liqueur glasses, pans and bowls). Decoration of a glass article lasted 10 to 30 sec depending on the surface area and the configuration of the deposited pattern. The article with the imposed stencil was put on a tournette that was rotated at a speed of 3 – 5 sec^{-1}. The sheet, plate, figured, and armored glass samples were held still before decorating, and the GN-5R plasma torch moved at a speed of 10 – 15 cm/sec in the course of spraying.

After plasma spraying, the macrostructure and properties of the decorative coatings were investigated. Upon hitting the substrate the particles are soldered to it but are not deformed significantly due to the high viscosity. A microscopic analysis of the deposited-layer macrostructure and the particle shape indicates that the glass grains are deformed insignificantly following impact against the substrate. The larger particles are deformed somewhat more due to their higher momentum and the greater amount of heat created at the point of contact with the substrate. Judging by the sizes of the surface layers torn from the substrate, it can be inferred that larger particles soften the surface layers at the point of contact to a greater depth than the smaller particles.

The strength of adhesion of the deposited glass particles to the substrate was determined by the break-off method [7]. Thus, with a thickness of the deposited layer equal to 350 μm, the strength of adhesion of the coating to the substrate was 12 ± 1.5 MPa. As the coating thickness increased, the strength of its adhesion to the base decreased. This is due to the scale factor and the level of residual stresses accumulated in the coating.

The heat resistance of household glassware with decorative coatings was investigated in accordance with GOST 26821–86. The experiments showed that the decorative plasma coatings satisfy the requirements of the standard.

Thus, plasma spraying of a glass powder on a glass substrate produces a decorative coating of a granular structure with good consumer properties. Virtually any crushed cullet waste can be used to decorate glass articles.

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